

**(Z)-Ethyl 3-[bis(4-chloro-3-ethyl-1-methyl-1*H*-pyrazol-5-ylcarbonyl)amino]-3-(4-chlorophenyl)-2-cyanopropanoate**Dehua Zhang,<sup>a\*</sup> Xiaoyan Zhang<sup>b</sup> and Lijuan Guo<sup>c</sup><sup>a</sup>Department of Chemistry and Environmental Engineering, Hubei Normal University, Huangshi 435002, People's Republic of China, <sup>b</sup>School of Mathematics and Physics, Huangshi Institute of Technology, Huangshi 435003, People's Republic of China, and <sup>c</sup>Department of Chemistry, Changsha Medical University, Changsha 410219, People's Republic of China

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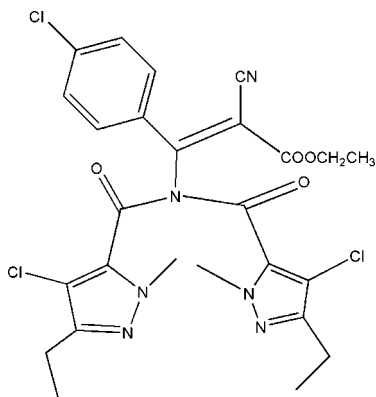
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å; disorder in main residue;  $R$  factor = 0.065;  $wR$  factor = 0.170; data-to-parameter ratio = 14.1.

The title compound,  $\text{C}_{26}\text{H}_{25}\text{Cl}_3\text{N}_6\text{O}_4$ , was prepared by the reaction of (*Z*)-ethyl 3-amino-3-(4-chlorophenyl)-2-cyanoacrylate and 4-chloro-3-ethyl-1-methyl-1*H*-pyrazole-5-carbonyl chloride. The dihedral angles between the chlorobenzene and the two pyrazole rings are  $59.8$  (2) and  $33.3$  (2)°. The two pyrazole rings are oriented to each other at a dihedral angle of  $84.7$  (2)°. The crystal packing is governed by intermolecular  $\text{C}-\text{H}\cdots\text{O}$  interactions, resulting in a three-dimensional network. The ethyl groups are disordered over two positions, with site-occupancy factors of 0.71/0.29 and 0.51/0.49.

**Related literature**

Several novel acrylate compounds are useful as inhibitors of *Pyricularia oryzae*, *Rhizoctonia solani*, *Botrytis cinerea* and *Gibberella zeae*; see: Heller *et al.* (2004); Creagh & Hubbell (1992); Ibers & Hamilton (1964).

**Experimental***Crystal data*

$\text{C}_{26}\text{H}_{25}\text{Cl}_3\text{N}_6\text{O}_4$   
 $M_r = 591.87$   
 Monoclinic,  $P2_1/c$   
 $a = 10.7277$  (3) Å  
 $b = 16.1476$  (5) Å  
 $c = 17.3109$  (5) Å  
 $\beta = 107.671$  (2)°

$V = 2857.21$  (14) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.36$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.20 \times 0.10 \times 0.10$  mm

*Data collection*

Bruker SMART CCD area-detector diffractometer  
 Absorption correction: none  
 18010 measured reflections

5600 independent reflections  
 3595 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.045$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.065$   
 $wR(F^2) = 0.170$   
 $S = 1.02$   
 5600 reflections  
 397 parameters

12 restraints  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.33$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.21$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{Cl13}-\text{H13}\cdots\text{O2}^i$	0.93	2.59	3.420 (5)	149

Symmetry code: (i)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ .

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

We thank the Hubei Normal University and the Hunan Provincial Natural Science Fund of China for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2113).

**References**

- Bruker (1997). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.  
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 Heller, D., Drexler, H. J., You, J. & Zhang, S. L. (2004). WO Patent 011414.  
 Ibers, J. A. & Hamilton, W. C. (1964). *Acta Cryst.* **17**, 781–782.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

**supplementary materials**

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**(Z)-Ethyl 3-[bis(4-chloro-3-ethyl-1-methyl-1*H*-pyrazol-5-ylcarbonyl)amino]-3-(4-chlorophenyl)-2-cyanopropanoate**

**D. Zhang, X. Zhang and L. Guo**

**Comment**

Recently, 2-cyanoacrylates have been in widespread used as agrochemicals because of their unique mechanism of action and good environmental profiles. The title compound is useful as an inhibitor of *Pyricularia oryzae*, *Rhizoctonia solani*, *Botrytis cinerea* and *Gibberella zeae* (Heller *et al.*, 2004; Ibers & Hamilton, 1964). In the title compound (Fig. 1), all bond lengths and angles are unexceptional. The planar chlorobenzene ring is approximately perpendicular to one of the pyrazole ring with a dihedral angle of 59.9 (2)°. The dihedral angle between this chlorobenzene ring and the other pyrazole rings is 33.3 (12)°. The dihedral angle between the two pyrazole rings is 84.7 (2)°. The crystal packing is governed by C—H···O intermolecular interactions resulting in a three-dimensional network (Table 1.). The ethyl groups are disordered over two positions, with site-occupancy factors of 0.71/0.29 and 0.51/0.49.

**Experimental**

To a solution of (*Z*)-ethyl 3-amino-3-(4-chlorophenyl)-2-cyanoacrylate (1.25 g, 0.0050 mol) in C<sub>1</sub>H<sub>2</sub>Cl<sub>2</sub>(18 ml), 4-chloro-3-ethyl-1-methyl-1*H*-pyrazole-5-carbonyl chloride (3.11 g, 0.015 mol) was added. Subsequently, Et<sub>3</sub>N<sub>1</sub>(1.52 g, 0.015 mol) was dropped into the solution under stirring. The reaction mixture was then heated to reflux, stirred for 4 h. Subsequently, it was cooled to room temperature. The reaction solution was filtered off and some white solid was separated. The organic phase was washed with water and then dried over Na<sub>2</sub>S<sub>1</sub>O<sub>4</sub>. After removal of the solvent, a brown dope was obtained. After column chromatogram using ethylacetate/light petroleum (1:6) as the eluent, small single crystals were grown from a solution of ethyl acetate/petroleum ether(3:1) after 45 days, at room temperature.

**Refinement**

Methyl H atoms were placed in calculated positions with C—H=0.96Å and the torsion angle was refined to fit the electron density; thermal parameters were refined as  $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{C})$ . Other H atoms were placed in calculated positions with C—H=0.96Å (methylene C—H) and 0.93Å (aromatic C—H), and refined in riding mode, with  $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$ .

**Figures**

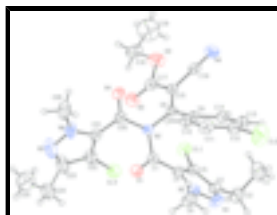


Fig. 1. The molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme. Only the higher occupied of the disordered sites is shown.

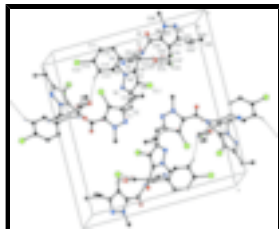


Fig. 2. The packing of the title compound, viewed down the *c*-axis.

**(Z)-Ethyl 3-[bis(4-chloro-3-ethyl-1-methyl-1*H*-pyrazol-5-ylcarbonyl)amino]-3-(4-chlorophenyl)-2-cyanopropanoate**

*Crystal data*

$C_{26}H_{25}Cl_3N_6O_4$

$M_r = 591.87$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 10.7277$  (3) Å

$b = 16.1476$  (5) Å

$c = 17.3109$  (5) Å

$\beta = 107.671$  (2)°

$V = 2857.21$  (14) Å<sup>3</sup>

$Z = 4$

$F_{000} = 1224$

$D_x = 1.376$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 2499 reflections

$\theta = 2.4$ – $20.2$ °

$\mu = 0.36$  mm<sup>-1</sup>

$T = 298$  K

Block, colorless

$0.20 \times 0.10 \times 0.10$  mm

*Data collection*

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298$  K

$\varphi$  and  $\omega$  scans

Absorption correction: none

18010 measured reflections

5600 independent reflections

3595 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.045$

$\theta_{max} = 26.0$ °

$\theta_{min} = 1.8$ °

$h = -13$ → $13$

$k = -14$ → $19$

$l = -19$ → $21$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.065$

$wR(F^2) = 0.170$

$S = 1.02$

5600 reflections

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0809P)^2 + 0.6207P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.33$  e Å<sup>-3</sup>

397 parameters

$$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$$

12 restraints

Extinction correction: none

Primary atom site location: structure-invariant direct methods

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.5605 (5)	1.1026 (3)	0.0809 (3)	0.1016 (16)	
H1A	0.4925	1.0742	0.0957	0.152*	
H1B	0.5308	1.1155	0.0241	0.152*	
H1C	0.5823	1.1529	0.1116	0.152*	
C2	0.6797 (4)	1.0481 (3)	0.0986 (2)	0.0819 (12)	
H2A	0.6586	0.9991	0.0647	0.098*	
H2B	0.7485	1.0777	0.0846	0.098*	
C3	0.7296 (4)	1.0218 (2)	0.1857 (2)	0.0600 (9)	
C4	0.7612 (3)	0.9620 (2)	0.30584 (19)	0.0464 (8)	
C5	0.6770 (3)	0.9653 (2)	0.22757 (19)	0.0493 (8)	
C6	0.9700 (4)	1.0424 (3)	0.3756 (3)	0.0843 (13)	
H6A	0.9397	1.0573	0.4205	0.126*	
H6B	1.0117	1.0893	0.3598	0.126*	
H6C	1.0316	0.9977	0.3913	0.126*	
C7	0.7665 (3)	0.91302 (19)	0.37875 (18)	0.0446 (7)	
C8	0.5482 (3)	0.96134 (19)	0.37330 (17)	0.0416 (7)	
C9	0.6001 (3)	1.0460 (2)	0.39174 (18)	0.0434 (7)	
C10	0.6964 (3)	1.0615 (2)	0.46510 (19)	0.0518 (8)	
H10	0.7256	1.0188	0.5023	0.062*	
C11	0.7483 (4)	1.1396 (3)	0.4827 (2)	0.0675 (10)	
H11	0.8112	1.1505	0.5320	0.081*	
C12	0.7058 (4)	1.2011 (2)	0.4263 (3)	0.0680 (11)	
C13	0.6112 (4)	1.1884 (2)	0.3540 (2)	0.0641 (10)	
H13	0.5830	1.2315	0.3173	0.077*	
C14	0.5585 (3)	1.1101 (2)	0.3366 (2)	0.0508 (8)	
H14	0.4946	1.1003	0.2875	0.061*	
C15	0.4182 (3)	0.9445 (2)	0.34745 (18)	0.0452 (7)	
C16	0.3269 (3)	1.0107 (2)	0.3428 (2)	0.0504 (8)	
C17	0.3619 (3)	0.8606 (3)	0.3228 (2)	0.0543 (9)	

## supplementary materials

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C20	0.6330 (3)	0.8337 (2)	0.44703 (19)	0.0479 (8)	
C21	0.7060 (3)	0.7572 (2)	0.44792 (19)	0.0491 (8)	
C22	0.7445 (4)	0.7138 (2)	0.3903 (2)	0.0604 (9)	
C23	0.8073 (5)	0.6430 (3)	0.4273 (3)	0.0923 (14)	
C18	0.1713 (16)	0.7798 (7)	0.2921 (11)	0.077 (5)	0.51
H18A	0.2076	0.7451	0.2585	0.093*	0.51
H18B	0.1817	0.7522	0.3435	0.093*	0.51
C19	0.0337 (14)	0.7994 (15)	0.2510 (13)	0.159 (9)	0.51
H19A	-0.0021	0.8289	0.2876	0.238*	0.51
H19B	-0.0145	0.7491	0.2343	0.238*	0.51
H19C	0.0275	0.8332	0.2044	0.238*	0.51
C24	0.8921 (8)	0.5836 (4)	0.3948 (5)	0.089 (2)	0.71
H24A	0.8987	0.6030	0.3431	0.107*	0.71
H24B	0.9794	0.5793	0.4327	0.107*	0.71
C25	0.8247 (9)	0.5025 (4)	0.3851 (6)	0.127 (3)	0.71
H25A	0.8184	0.4845	0.4366	0.191*	0.71
H25B	0.8735	0.4626	0.3650	0.191*	0.71
H25C	0.7385	0.5079	0.3474	0.191*	0.71
C26	0.7327 (5)	0.7275 (3)	0.5962 (2)	0.0921 (14)	
H26A	0.6420	0.7356	0.5914	0.138*	
H26B	0.7811	0.7764	0.6186	0.138*	
H26C	0.7660	0.6812	0.6312	0.138*	
Cl1	0.53576 (9)	0.91015 (6)	0.18601 (5)	0.0620 (3)	
Cl2	0.77506 (16)	1.29995 (8)	0.44793 (10)	0.1232 (6)	
Cl3	0.71509 (10)	0.73843 (6)	0.29021 (5)	0.0700 (3)	
N1	0.8404 (3)	1.0541 (2)	0.23522 (19)	0.0693 (9)	
N2	0.8587 (3)	1.01616 (19)	0.30722 (17)	0.0596 (8)	
N3	0.6432 (2)	0.89762 (15)	0.39096 (14)	0.0414 (6)	
N4	0.2531 (3)	1.0622 (2)	0.3401 (2)	0.0723 (9)	
N5	0.8081 (4)	0.6418 (2)	0.5053 (2)	0.0992 (13)	
N6	0.7463 (3)	0.71124 (19)	0.51636 (17)	0.0667 (8)	
O1	0.8667 (2)	0.88843 (15)	0.42578 (14)	0.0596 (6)	
O2	0.4232 (2)	0.79961 (16)	0.31937 (17)	0.0697 (7)	
O3	0.2329 (2)	0.86236 (17)	0.30416 (18)	0.0849 (9)	
O4	0.5658 (2)	0.84529 (16)	0.48997 (14)	0.0683 (7)	
C19'	0.0535 (17)	0.7807 (15)	0.2940 (10)	0.123 (8)	0.49
H19D	0.0884	0.7667	0.3504	0.184*	0.49
H19E	-0.0025	0.7369	0.2658	0.184*	0.49
H19F	0.0041	0.8311	0.2885	0.184*	0.49
C18'	0.160 (2)	0.7920 (11)	0.2596 (11)	0.099 (7)	0.49
H18C	0.1275	0.8040	0.2020	0.119*	0.49
H18D	0.2153	0.7430	0.2675	0.119*	0.49
C24'	0.8165 (13)	0.5613 (7)	0.3901 (10)	0.064 (4)	0.29
H24C	0.7551	0.5582	0.3359	0.077*	0.29
H24D	0.7973	0.5170	0.4226	0.077*	0.29
C25'	0.9573 (15)	0.5544 (12)	0.3871 (14)	0.114 (8)	0.29
H25D	0.9900	0.6086	0.3813	0.171*	0.29
H25E	0.9590	0.5206	0.3418	0.171*	0.29
H25F	1.0110	0.5296	0.4364	0.171*	0.29

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.120 (4)	0.103 (4)	0.069 (3)	0.023 (3)	0.010 (3)	0.017 (3)
C2	0.106 (3)	0.090 (3)	0.058 (2)	0.009 (3)	0.037 (2)	0.017 (2)
C3	0.068 (2)	0.067 (2)	0.053 (2)	0.007 (2)	0.0323 (19)	0.0092 (18)
C4	0.0394 (17)	0.057 (2)	0.0489 (18)	0.0009 (15)	0.0223 (14)	0.0042 (15)
C5	0.0530 (19)	0.054 (2)	0.0459 (18)	0.0040 (16)	0.0219 (15)	0.0022 (15)
C6	0.051 (2)	0.114 (4)	0.085 (3)	-0.023 (2)	0.016 (2)	0.016 (3)
C7	0.0445 (18)	0.0460 (19)	0.0444 (17)	-0.0024 (15)	0.0150 (14)	-0.0006 (14)
C8	0.0415 (17)	0.0505 (19)	0.0354 (15)	0.0011 (14)	0.0156 (13)	0.0014 (13)
C9	0.0433 (17)	0.0491 (19)	0.0426 (17)	0.0016 (14)	0.0202 (14)	0.0013 (15)
C10	0.060 (2)	0.055 (2)	0.0413 (17)	0.0009 (17)	0.0167 (15)	0.0000 (16)
C11	0.072 (2)	0.072 (3)	0.058 (2)	-0.015 (2)	0.0188 (19)	-0.016 (2)
C12	0.081 (3)	0.046 (2)	0.087 (3)	-0.013 (2)	0.041 (2)	-0.014 (2)
C13	0.074 (2)	0.052 (2)	0.070 (2)	0.0044 (19)	0.027 (2)	0.0065 (19)
C14	0.0527 (19)	0.052 (2)	0.0491 (19)	0.0011 (16)	0.0172 (15)	0.0026 (16)
C15	0.0468 (18)	0.0497 (19)	0.0441 (17)	-0.0018 (15)	0.0213 (14)	0.0034 (15)
C16	0.0428 (18)	0.056 (2)	0.056 (2)	-0.0021 (17)	0.0206 (15)	0.0040 (17)
C17	0.049 (2)	0.066 (3)	0.0500 (19)	-0.0080 (18)	0.0183 (15)	-0.0022 (17)
C20	0.0542 (19)	0.049 (2)	0.0430 (17)	-0.0028 (16)	0.0180 (15)	0.0033 (15)
C21	0.056 (2)	0.047 (2)	0.0459 (18)	-0.0028 (16)	0.0180 (15)	0.0041 (15)
C22	0.074 (2)	0.055 (2)	0.052 (2)	0.0086 (18)	0.0182 (18)	0.0001 (17)
C23	0.140 (4)	0.065 (3)	0.074 (3)	0.039 (3)	0.034 (3)	0.001 (2)
C18	0.057 (7)	0.081 (8)	0.099 (11)	-0.032 (6)	0.031 (7)	-0.017 (7)
C19	0.083 (10)	0.159 (17)	0.20 (2)	-0.053 (9)	-0.012 (13)	-0.026 (17)
C24	0.096 (7)	0.066 (5)	0.106 (6)	0.006 (5)	0.030 (6)	-0.002 (4)
C25	0.169 (9)	0.088 (6)	0.144 (8)	-0.016 (6)	0.076 (6)	-0.025 (6)
C26	0.147 (4)	0.079 (3)	0.053 (2)	0.015 (3)	0.034 (3)	0.016 (2)
Cl1	0.0643 (6)	0.0700 (6)	0.0486 (5)	-0.0069 (4)	0.0125 (4)	-0.0022 (4)
Cl2	0.1617 (14)	0.0646 (8)	0.1425 (13)	-0.0441 (8)	0.0452 (10)	-0.0271 (8)
Cl3	0.0878 (7)	0.0770 (7)	0.0490 (5)	0.0122 (5)	0.0263 (5)	-0.0028 (5)
N1	0.068 (2)	0.085 (2)	0.064 (2)	-0.0108 (18)	0.0332 (17)	0.0137 (18)
N2	0.0485 (16)	0.075 (2)	0.0597 (18)	-0.0044 (15)	0.0225 (14)	0.0099 (16)
N3	0.0416 (14)	0.0435 (15)	0.0420 (13)	-0.0004 (12)	0.0172 (11)	0.0034 (12)
N4	0.0542 (19)	0.074 (2)	0.094 (2)	0.0064 (17)	0.0310 (17)	0.0015 (19)
N5	0.154 (4)	0.066 (2)	0.073 (2)	0.041 (2)	0.027 (2)	0.0145 (19)
N6	0.098 (2)	0.0534 (19)	0.0487 (17)	0.0085 (17)	0.0219 (16)	0.0094 (15)
O1	0.0428 (13)	0.0702 (16)	0.0600 (14)	0.0027 (11)	0.0069 (11)	0.0128 (12)
O2	0.0635 (16)	0.0582 (17)	0.0903 (19)	-0.0093 (14)	0.0278 (14)	-0.0143 (14)
O3	0.0497 (15)	0.082 (2)	0.120 (2)	-0.0187 (14)	0.0214 (15)	-0.0215 (18)
O4	0.0842 (17)	0.0763 (18)	0.0597 (15)	0.0154 (14)	0.0445 (14)	0.0172 (13)
C19'	0.134 (18)	0.129 (14)	0.128 (14)	-0.063 (14)	0.072 (12)	-0.039 (12)
C18'	0.074 (10)	0.100 (10)	0.122 (15)	-0.028 (7)	0.027 (10)	-0.012 (10)
C24'	0.067 (10)	0.043 (9)	0.081 (10)	-0.003 (8)	0.020 (9)	-0.007 (8)
C25'	0.097 (15)	0.124 (18)	0.142 (17)	0.032 (13)	0.068 (13)	-0.024 (14)

## supplementary materials

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### *Geometric parameters (Å, °)*

C1—C2	1.505 (6)	C20—C21	1.460 (5)
C1—H1A	0.9600	C21—N6	1.353 (4)
C1—H1B	0.9600	C21—C22	1.381 (5)
C1—H1C	0.9600	C22—C23	1.382 (6)
C2—C3	1.499 (5)	C22—C13	1.710 (4)
C2—H2A	0.9700	C23—N5	1.348 (5)
C2—H2B	0.9700	C23—C24'	1.484 (9)
C3—N1	1.343 (5)	C23—C24	1.542 (7)
C3—C5	1.387 (5)	C18—C19	1.465 (10)
C4—N2	1.358 (4)	C18—O3	1.475 (8)
C4—C5	1.383 (4)	C18—H18A	0.9700
C4—C7	1.476 (4)	C18—H18B	0.9700
C5—C11	1.716 (3)	C19—H19A	0.9600
C6—N2	1.465 (5)	C19—H19B	0.9600
C6—H6A	0.9600	C19—H19C	0.9600
C6—H6B	0.9600	C24—C25	1.481 (7)
C6—H6C	0.9600	C24—H24A	0.9700
C7—O1	1.202 (3)	C24—H24B	0.9700
C7—N3	1.423 (4)	C25—H25A	0.9600
C8—C15	1.356 (4)	C25—H25B	0.9600
C8—N3	1.415 (4)	C25—H25C	0.9600
C8—C9	1.475 (4)	C26—N6	1.457 (5)
C9—C14	1.387 (4)	C26—H26A	0.9600
C9—C10	1.395 (4)	C26—H26B	0.9600
C10—C11	1.376 (5)	C26—H26C	0.9600
C10—H10	0.9300	N1—N2	1.349 (4)
C11—C12	1.370 (6)	N5—N6	1.345 (4)
C11—H11	0.9300	O3—C18'	1.458 (9)
C12—C13	1.367 (5)	C19'—C18'	1.456 (10)
C12—C12	1.752 (4)	C19'—H19D	0.9600
C13—C14	1.379 (5)	C19'—H19E	0.9600
C13—H13	0.9300	C19'—H19F	0.9600
C14—H14	0.9300	C18'—H18C	0.9700
C15—C16	1.436 (5)	C18'—H18D	0.9700
C15—C17	1.491 (5)	C24'—C25'	1.531 (10)
C16—N4	1.139 (4)	C24'—H24C	0.9700
C17—O2	1.196 (4)	C24'—H24D	0.9700
C17—O3	1.323 (4)	C25'—H25D	0.9600
C20—O4	1.197 (4)	C25'—H25E	0.9600
C20—N3	1.444 (4)	C25'—H25F	0.9600
C2—C1—H1A	109.5	C16—C15—C17	116.7 (3)
C2—C1—H1B	109.5	N4—C16—C15	178.5 (4)
H1A—C1—H1B	109.5	O2—C17—O3	123.8 (3)
C2—C1—H1C	109.5	O2—C17—C15	125.5 (3)
H1A—C1—H1C	109.5	O3—C17—C15	110.7 (3)
H1B—C1—H1C	109.5	O4—C20—N3	119.2 (3)



C3—C2—C1	113.1 (3)	O4—C20—C21	123.3 (3)
C3—C2—H2A	109.0	N3—C20—C21	117.5 (3)
C1—C2—H2A	109.0	N6—C21—C22	105.6 (3)
C3—C2—H2B	109.0	N6—C21—C20	120.0 (3)
C1—C2—H2B	109.0	C22—C21—C20	134.3 (3)
H2A—C2—H2B	107.8	C21—C22—C23	107.1 (3)
N1—C3—C5	110.1 (3)	C21—C22—Cl3	127.6 (3)
N1—C3—C2	120.5 (3)	C22—C21—C20	134.3 (3)
C5—C3—C2	129.4 (4)	C21—C22—C23	107.1 (3)
N2—C4—C5	105.2 (3)	C21—C22—Cl3	127.6 (3)
N2—C4—C7	120.0 (3)	C23—C22—Cl3	125.2 (3)
C5—C4—C7	134.7 (3)	N5—C23—C22	109.3 (3)
C4—C5—C3	106.8 (3)	N5—C23—C24'	116.2 (8)
C4—C5—Cl1	128.4 (3)	C22—C23—C24'	128.4 (8)
C3—C5—Cl1	124.7 (3)	N5—C23—C24	122.2 (5)
N2—C6—H6A	109.5	C22—C23—C24	127.2 (5)
N2—C6—H6B	109.5	C19—C18—O3	102.4 (8)
H6A—C6—H6B	109.5	C19—C18—H18A	111.3
N2—C6—H6C	109.5	O3—C18—H18A	111.3
H6A—C6—H6C	109.5	C19—C18—H18B	111.3
H6B—C6—H6C	109.5	O3—C18—H18B	111.3
O1—C7—N3	121.5 (3)	H18A—C18—H18B	109.2
O1—C7—C4	123.4 (3)	C25—C24—C23	105.6 (6)
N3—C7—C4	115.1 (3)	C25—C24—H24A	110.6
C15—C8—N3	121.8 (3)	C23—C24—H24A	110.6
C15—C8—C9	122.7 (3)	C25—C24—H24B	110.6
N3—C8—C9	115.3 (2)	C23—C24—H24B	110.6
C14—C9—C10	119.2 (3)	H24A—C24—H24B	108.7
C14—C9—C8	121.5 (3)	N6—C26—H26A	109.5
C10—C9—C8	119.3 (3)	N6—C26—H26B	109.5
C11—C10—C9	120.3 (3)	H26A—C26—H26B	109.5
C11—C10—H10	119.9	N6—C26—H26C	109.5
C9—C10—H10	119.9	H26A—C26—H26C	109.5
C12—C11—C10	118.8 (3)	H26B—C26—H26C	109.5
C12—C11—H11	120.6	C3—N1—N2	105.4 (3)
C10—C11—H11	120.6	N1—N2—C4	112.4 (3)
C13—C12—C11	122.5 (3)	N1—N2—C6	118.0 (3)
C13—C12—Cl2	118.8 (3)	C4—N2—C6	129.4 (3)
C11—C12—Cl2	118.7 (3)	C8—N3—C7	118.8 (2)
C12—C13—C14	118.6 (4)	C8—N3—C20	117.9 (2)
C12—C13—H13	120.7	C7—N3—C20	119.2 (2)
C14—C13—H13	120.7	N6—N5—C23	106.1 (3)
C13—C14—C9	120.6 (3)	N5—N6—C21	111.9 (3)
C13—C14—H14	119.7	N5—N6—C26	118.7 (3)
C9—C14—H14	119.7	C21—N6—C26	129.4 (3)
C8—C15—C16	119.0 (3)	C17—O3—C18'	117.5 (10)
C8—C15—C17	124.3 (3)	C17—O3—C18	114.0 (8)
C16—C15—C17	116.7 (3)	C18'—C19'—H19D	109.5
N4—C16—C15	178.5 (4)	C18'—C19'—H19E	109.5

## supplementary materials

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O2—C17—O3	123.8 (3)	H19D—C19'—H19E	109.5
O2—C17—C15	125.5 (3)	C18'—C19'—H19F	109.5
O3—C17—C15	110.7 (3)	H19D—C19'—H19F	109.5
O4—C20—N3	119.2 (3)	H19E—C19'—H19F	109.5
O4—C20—C21	123.3 (3)	C19'—C18'—O3	103.9 (9)
N3—C20—C21	117.5 (3)	C19'—C18'—H18C	111.0
N6—C21—C22	105.6 (3)	O3—C18'—H18C	111.0
N6—C21—C20	120.0 (3)	C19'—C18'—H18D	111.0
C22—C21—C20	134.3 (3)	O3—C18'—H18D	111.0
C21—C22—C23	107.1 (3)	H18C—C18'—H18D	109.0
C21—C22—C13	127.6 (3)	C23—C24'—C25'	106.0 (8)
C10—C11—H11	120.6	C23—C24'—H24C	110.5
C13—C12—C11	122.5 (3)	C25'—C24'—H24C	110.5
C13—C12—C12	118.8 (3)	C23—C24'—H24D	110.5
C11—C12—C12	118.7 (3)	C25'—C24'—H24D	110.5
C12—C13—C14	118.6 (4)	H24C—C24'—H24D	108.7
C12—C13—H13	120.7	C24'—C25'—H25D	109.5
C14—C13—H13	120.7	C24'—C25'—H25E	109.5
C13—C14—C9	120.6 (3)	H25D—C25'—H25E	109.5
C13—C14—H14	119.7	C24'—C25'—H25F	109.5
C9—C14—H14	119.7	H25D—C25'—H25F	109.5
C8—C15—C16	119.0 (3)	H25E—C25'—H25F	109.5
C8—C15—C17	124.3 (3)		
C1—C2—C3—N1	-107.3 (5)	C13—C22—C23—C24'	-26.2 (10)
C1—C2—C3—C5	72.6 (6)	C21—C22—C23—C24	-166.6 (5)
N2—C4—C5—C3	0.2 (4)	C13—C22—C23—C24	16.2 (8)
C7—C4—C5—C3	-176.8 (3)	N5—C23—C24—C25	76.6 (8)
N2—C4—C5—C11	178.8 (2)	C22—C23—C24—C25	-118.3 (7)
C7—C4—C5—C11	1.8 (6)	C24'—C23—C24—C25	-12.9 (14)
N1—C3—C5—C4	-1.2 (4)	C5—C3—N1—N2	1.6 (4)
C2—C3—C5—C4	178.9 (4)	C2—C3—N1—N2	-178.4 (3)
N1—C3—C5—C11	-179.8 (3)	C3—N1—N2—C4	-1.6 (4)
C2—C3—C5—C11	0.2 (6)	C3—N1—N2—C6	-176.7 (3)
N2—C4—C7—O1	-33.8 (5)	C5—C4—N2—N1	0.8 (4)
C5—C4—C7—O1	142.9 (4)	C7—C4—N2—N1	178.4 (3)
N2—C4—C7—N3	145.1 (3)	C5—C4—N2—C6	175.3 (4)
C5—C4—C7—N3	-38.2 (5)	C7—C4—N2—C6	-7.1 (5)
C15—C8—C9—C14	-51.9 (4)	C15—C8—N3—C7	149.4 (3)
N3—C8—C9—C14	133.3 (3)	C9—C8—N3—C7	-35.7 (4)
C15—C8—C9—C10	130.3 (3)	C15—C8—N3—C20	-53.3 (4)
N3—C8—C9—C10	-44.5 (4)	C9—C8—N3—C20	121.6 (3)
C14—C9—C10—C11	0.7 (5)	O1—C7—N3—C8	140.0 (3)
C8—C9—C10—C11	178.5 (3)	C4—C7—N3—C8	-38.9 (4)
C9—C10—C11—C12	-1.4 (5)	O1—C7—N3—C20	-17.0 (4)
C10—C11—C12—C13	1.7 (6)	C4—C7—N3—C20	164.1 (3)
C10—C11—C12—C12	-178.5 (3)	O4—C20—N3—C8	-16.6 (4)
C11—C12—C13—C14	-1.3 (6)	C21—C20—N3—C8	163.2 (3)
C12—C12—C13—C14	178.9 (3)	O4—C20—N3—C7	140.6 (3)
C12—C13—C14—C9	0.5 (5)	C21—C20—N3—C7	-39.6 (4)

C10—C9—C14—C13	-0.2 (5)	C22—C23—N5—N6	0.0 (6)
C8—C9—C14—C13	-178.0 (3)	C24'—C23—N5—N6	-154.8 (7)
N3—C8—C15—C16	170.3 (3)	C24—C23—N5—N6	167.5 (5)
C9—C8—C15—C16	-4.3 (4)	C23—N5—N6—C21	-0.2 (5)
N3—C8—C15—C17	-9.9 (5)	C23—N5—N6—C26	-179.5 (4)
C9—C8—C15—C17	175.6 (3)	C22—C21—N6—N5	0.2 (4)
C8—C15—C17—O2	-3.5 (5)	C20—C21—N6—N5	178.0 (3)
C16—C15—C17—O2	176.4 (3)	C22—C21—N6—C26	179.5 (4)
C8—C15—C17—O3	177.0 (3)	C20—C21—N6—C26	-2.8 (6)
C16—C15—C17—O3	-3.1 (4)	O2—C17—O3—C18'	-14.9 (10)
O4—C20—C21—N6	-27.8 (5)	C15—C17—O3—C18'	164.7 (9)
N3—C20—C21—N6	152.4 (3)	O2—C17—O3—C18	9.9 (9)
O4—C20—C21—C22	149.1 (4)	C15—C17—O3—C18	-170.5 (8)
N3—C20—C21—C22	-30.7 (5)	C19—C18—O3—C17	-164.7 (12)
N6—C21—C22—C23	-0.2 (4)	C19—C18—O3—C18'	-60 (4)
C20—C21—C22—C23	-177.4 (4)	C17—O3—C18'—C19'	142.5 (12)
N6—C21—C22—C13	176.9 (3)	C18—O3—C18'—C19'	56 (4)
C20—C21—C22—C13	-0.3 (6)	N5—C23—C24'—C25'	-103.8 (14)
C21—C22—C23—N5	0.1 (6)	C22—C23—C24'—C25'	107.0 (14)
C13—C22—C23—N5	-177.1 (3)	C24—C23—C24'—C25'	5.7 (12)
C21—C22—C23—C24'	151.0 (8)		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C13—H13 $\cdots$ O2 <sup>i</sup>	0.93	2.59	3.420 (5)	149

Symmetry codes: (i)  $-x+1, y+1/2, -z+1/2$ .

Fig. 1

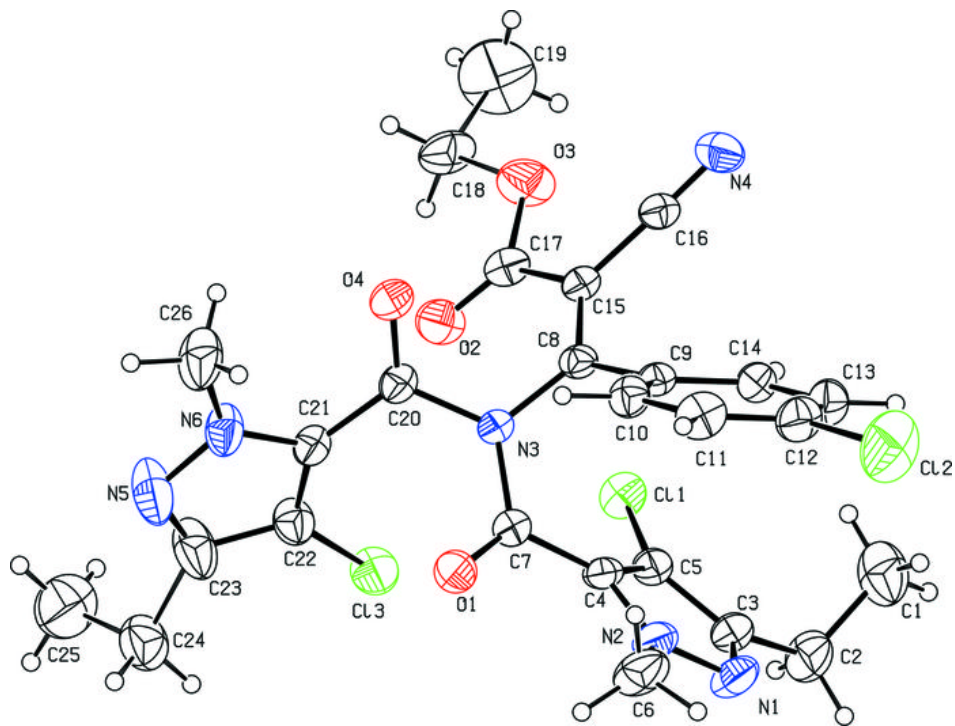


Fig. 2

